

**ETHANOL DRY REFORMING  
OVER Ce-PROMOTED Ni/Al<sub>2</sub>O<sub>3</sub> CATALYST  
FOR H<sub>2</sub> PRODUCTION**

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## ABSTRACT

Ethanol dry reforming show a high potential to become a technology used to produce alternative fuel a transition from traditional petroleum based fuel which continue to increase in price along with its depletion. The product gas is called syngas that consists of CO and H<sub>2</sub> gasses, whereby H<sub>2</sub> can be used as a clean energy carrier that could help to reduce the emission of GHG. The major problem faced in this process is catalyst deactivation by coking or carbon deposition therefore a lot of effort had been done in researched of catalyst that able to prolong the reaction and also economically feasible. Recently a non noble metal Nickel (Ni) had been a great interest for catalyst for the industrial application because of its cheap in price and high C-C bond breaking activity. The results from characterization of the catalyst based on XRD analysis the calcinations and the addition of Ce promoter did not alter the composition of the catalyst hence the results show consistency with the reading from the data base. TGA analysis illustrates the addition of Ce increase the height and shifts the peaks to the left. The cracks and small catalyst size from SEM results tells that alumina has high degree of dispersion and lastly from BET study the deposition of Ce increase the diameter of catalyst however it decreases the pores surface area. Based on reaction study results by manipulating the feed partial pressure of CO<sub>2</sub> at the highest of 50 kPa, the conversion of H<sub>2</sub> and CO<sub>2</sub> is at the highest up to 90 % for H<sub>2</sub>. The additions of quantity of CO<sub>2</sub> feed ratio allow further decomposition of methane (CH<sub>4</sub>) thus increase more amount of H<sub>2</sub> produced a consistent results with the theory. The results obtained from this research gave positive outcomes in the application of the process in industrial scale by increasing the feed ratio of CO<sub>2</sub> to 2.5 to ethanol more H<sub>2</sub> in being converted.

## ABSTRAK

Etanol kering pembaharuan menunjukkan potensi yang tinggi untuk menjadi teknologi yang akan digunakan untuk menghasilkan bahan api alternatif peralihan daripada bahan api tradisional berasaskan petroleum yang akan terus meningkat harga selari dengan kekurangan hasil bahan api tersebut. Gas produk dipanggil syngas yang terdiri daripada CO dan H<sub>2</sub> gas, di mana H<sub>2</sub> boleh digunakan sebagai pembawa tenaga bersih yang boleh membantu untuk mengurangkan pelepasan gas rumah hijau. Masalah utama yang dihadapi dalam proses ini adalah pemangkin penyahaktifan oleh pemendapan karbon disebabkan hal yang demikian banyak usaha telah dilakukan dalam kajian mangkin yang dapat memanjangkan tindak balas dan juga dilaksanakan dari segi ekonomi yang berpatutan. Sejak kebelakangan ini, logam tidak adi nikel (Ni) telah menjadi suatu kepentingan yang besar untuk pemangkin kepada aplikasi perindustrian kerana harga yang murah dan C-C leraian bon aktiviti yang tinggi. Hasil keputusan daripada pencirian mangkin berdasarkan analisis XRD yang pengkalsinan dan penambahan Ce sebagai pengalok pemangkin tidak mengubah komposisi pemangkin oleh itu hasil kajian menunjukkan konsistensi dengan bacaan dari pangkalan data. Analisis TGA menunjukkan penambahan Ce meningkatkan ketinggian puncak dan beralih puncak ke kiri. Retakan dan saiz pemangkin yang kecil dari kajian SEM menunjukkan bahawa alumina mempunyai kadar serakan tinggi dan akhir sekali kajian BET pemendapan Ce meningkatkan diameter pemangkin walau bagaimanapun ia mengurangkan luas permukaan liang. Berdasarkan hasil kajian tindak balas dengan memanipulasi nisbah punca tekanan CO<sub>2</sub> di tertinggi 50 kPa, penukaran H<sub>2</sub> dan CO<sub>2</sub> adalah di kedudukan paling tinggi sehingga 90% bagi H. Penambahan kuantiti punca nisbah CO<sub>2</sub> membolehkan penguraian ikatan metana (CH<sub>4</sub>) seterusnya meningkatkan lagi jumlah H<sub>2</sub> menghasilkan keputusan yang konsisten dengan teori. Hasil kajian yang diperolehi daripada kajian ini telah memberikan hasil yang positif dalam penggunaan proses dalam skala industri dengan meningkatkan punca nisbah gas CO<sub>2</sub> kepada 2.5 kepada etanol mampu menghasilkan gas H<sub>2</sub> dalam ditukarkan.

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## LIST OF ABBREVIATIONS

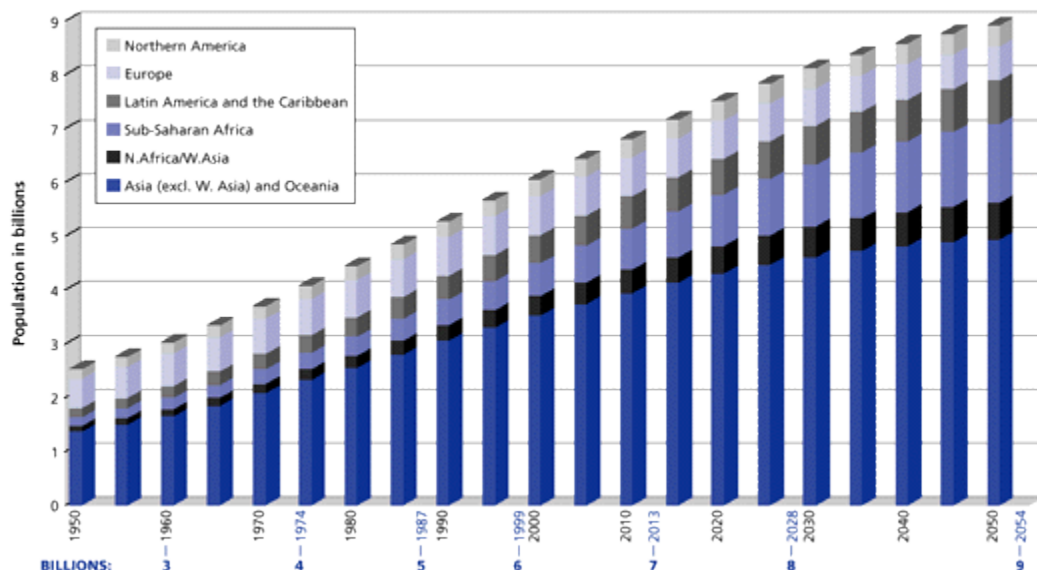
°C	Degree Celsius
Ce	Cerium
CH <sub>4</sub>	Methane
Co	Cobalt
CO <sub>2</sub>	Carbon dioxide
CO	Carbon monoxide
Cu	Copper
g	Gram
g/mol	Molar mass
H <sub>2</sub>	Hydrogen
K	Kelvin
Kg/m <sup>3</sup>	Density
KJmol <sup>-1</sup>	Energy
kWh	Power
Mpa	Mega pascal
Ni/Al <sub>2</sub> O <sub>3</sub>	Nickel alumina
Pt	Platinum
ppm	Part per million
RT10	Ramping 10 °C/min
RT15	Ramping 15 °C/min
RT20	Ramping 20 °C/min
ΔH°	Enthalpy
%	Percentage

<i>EDR</i>	Ethanol dry reforming
ESR	Ethanol steam reforming
BET	Brunauer, Emmett and Teller
GHG	Green house gas
NASA	National Aeronautics and Space Administration
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric analysis
USA	United State of America
IT	Information Technology
VS	Versus
XRD	X-ray Diffraction

# 1 INTRODUCTION

## 1.1 Background

Human population increase as much as 1.3 % ever year nonetheless this consider to be smaller compare to in 1965-1970 which is 2.1% (globalchange.umich.edu). In spite of that today at much larger population number it is consider as exponential growth rate and must be taken seriously. Experts acknowledge that the world's current rate of energy consumption is at alarming rate and will be lacking of power unless we find a new alternative form of renewable energy source to confront with the world energy crisis.



**Figure 1-1 : Projected world population growth**

According to The World Bank Working for a World Free of Poverty website 3 045.01 kWh of Earth electricity consumption per capita in 2011 compare to 2 582 kWh in 2004 approximately 17.9% increase over 6 years period(worldbank.org). The demands for electric power increase immensely especially in developing countries such as in China and South Korea to satisfy the energy requirement for their power plants.

The main challenge is not so much about whether oil will continue to exist, but whether there will be sufficient supplies at affordable prices. For countries such as the United States, who import from others countries for a steady supply of oil, availability and price will be their ultimatum. As oil or resources being use worldwide at rapid rate this lead to acutely surge the market price ([fueleconomy.gov](http://fueleconomy.gov))([eni.com](http://eni.com)).

In a sense of global issues however Middle-Eastern politics plays a major role here since there are a huge amount of energy resources available. These have become a great interest of western economies such as France, Britain, USA and former Soviet Union. Over the past decades Middle East had suffered wars, overthrow of democratically elected leaders, and puppet governments and dictatorships that all rotated around the world's energy crisis ([worldenergy.org](http://worldenergy.org)).

In conclusion hydrogen will be the new clean energy carrier to replace the world thirst of energy where hydrogen is use in fuel cell engine to provide power. Fuel cells will be available to a wide range of products, from a miniature size use in portable devices such as laptops and hand phones, to huge engine of cars, ships, and airplanes, likewise to provide power in industrial sector ([fuelcellenergy.com](http://fuelcellenergy.com)).

Additionally applying hydrogen in fuel cell systems emit no harmful emissions by products as a matter of facts NASA spaceships burned hydrogen gas leaving clean drinking water for the astronauts ([nasa.gov](http://nasa.gov)). They are also excellent in Medical and IT field since it make low noise and high power output. Hydrogen and Fuel Cells will serve a better future for both man and environment unlike other resources either toxic or harm to the environment.

## ***1.2 Motivation***

Currently as global demand of petroleum based energy increases exponentially each every year, a new more sustainable energy is highly desired. Thus transition from traditional petroleum based energy to hydrogen economy is one of the best solving answer, since hydrogen is a clean energy carrier (Xun Hu. 2014). Moreover, hydrogen is expected to be one of the most important fuels where it can be use in fuel cell to generate electricity and in hydrogen internal combustion engine vehicles (Murat CİNİVİZ. 2012). The benefits of it all are such as to reduce the dependence on non-renewable resources which are very costly and gradually to continue with it depletion, decrease in emissions of greenhouse gases (GHG) and others harmful air pollutions from the combustion of petroleum based fuel. Other than that hydrogen is also used widely in the production of pharmaceuticals, fine chemicals and bulk chemicals such as ammonia and methanol (Wenju Wang, 2009).

Hydrogen can be produced from diverse energy resources, using varieties of processes technologies such as thermochemical, biological, electrolytic, and photolytic. Bio-derived liquid (ethanol) undergo reforming, which is the most plausible way to produce hydrogen since ethanol is a non toxic nature substance, high availability, cheap and a renewable resource. 95% of ethanol production is by fermentation called bioethanol the raw products comes from various range of biomass resources such as cellulose of plant, argro-industrial wastes, forestry materials and municipal solid waste, in Canada they uses grains, Brazil; sugarcane and in the United State; corn. Apart from that ethanol is feasible for large scale production because it is easily to store, handle and transport due to its volatility. The dry reforming of ethanol reaction is as follows (A. Zawadzki.2014).

A non noble metal such as Ni is currently a great interest to be use as catalyst since Ni has high C-C bond breaking activity overall it is cheaper, compare to other noble metals such as Rh, Ru, Pd and Pt (Nader Rahemi. 2013). However the acid sites of  $\text{Al}_2\text{O}_3$  promote ethanol dehydration, Ni/ $\text{Al}_2\text{O}_3$  catalyst suffers carbon deposition. To subdue deactivation alkaline oxides such as MgO and CaO is use as additives by neutralizing the acidity, apart from that  $\text{ZrO}_2$  added to Ni/ $\text{Al}_2\text{O}_3$  catalyst to improve stability and boost adsorption and dissociation of water on the surface of nickel catalyst (Seung Ju Han. 2014).

The catalyst Ni/Al<sub>2</sub>O<sub>3</sub> is synthesis by wet impregnation process as it is most prefer in industrial level. The simplicity of the methodology and the convenience make impregnation method is attractive for industrial scale up purpose and much research has been dedicated to improving the preparation method.

Dry reforming or carbon reforming is a process used to produce syngas from reacting carbon dioxide with hydrocarbon or other volatile fossil fuels (K. De Oliveira-Vigier. 2008). It was first developed by Franz Fisher and Hans Tropsch in Germany in 1928. Their researched was mainly about production of syngas from coal and gaseous fuels and production liquid fuel from syngas, since Germany is a place with abundant supply of coal but scarce of petroleum.

### ***1.3 Problem statement***

21<sup>st</sup> century monumental dilemma is too much dependency on the limited fossil fuels where the use of fossil fuels consequencing high emission of harmful GHG disturbing the environment such as global warming.

### ***1.4 Objectives***

The following are the objectives of this research:

- Examine the effect of feed composition on 3%Ce-10%Ni/Al<sub>2</sub>O<sub>3</sub>.
- To investigate the effect of reaction condition such as feed composition and reaction temperature on catalytic selectivity and activity from ethanol dry reforming over 3%Ce-10%Ni/Al<sub>2</sub>O<sub>3</sub>.

## ***1.5 Scope of this research***

In order to achieve all the objectives, several scopes have been identified. First procedure is the pre-treatment of alumina( $\text{Al}_2\text{O}_3$ ) support, done by calcinations process at temperature of 600 °C for 5 hours. Secondly is the synthesis of catalyst, nickel(II) nitrate  $\text{Ni}(\text{NO}_3)_2$  dissolve in water and continuously stir for 3 hours and left to dry over night at 110 °C. Once dried the catalyst then undergo calcinations for 5 hours at 500 °C. Catalyst characterization will be conduct which are are Brunauer-Emmett-Teller (BET), Scanning Electron Microscopy (SEM), X-Ray Diffraction(XRD), and Temperature-Programmed Reduction (TPR). The gas product from the reaction will be test by Gas Chromatography (GC).

## ***1.6 Organisation of thesis***

This thesis is about the production of hydrogen gas from ethanol via dry reforming and it begins with the background and literature review. In chapter 2 literature review talks about fuel cells technology, production of hydrogen from renewable and non-renewable sources, comparison of ethanol dry reforming versus ethanol steam reforming and catalyst deactivation.

Chapter 3 discussed about materials used and methods for synthesizing the catalyst. Catalysts (10%-Ni/ $\text{Al}_2\text{O}_3$  and 3%Ce-10%Ni/ $\text{Al}_2\text{O}_3$ ) were prepared via wetness impregnation is illustrated using flow chart. Calculation on how to measure the right amount of catalyst for synthesizing is also shown in this chapter.

Chapter 4 includes results from the two catalysts characterization. In this chapter also include the results from preliminary runs of reaction study that are detailed. Where the reactions were conducted at fixed temperature and pressure but manipulated partial pressure and catalysts used.

Chapter 5 provides the overall results finding for the thesis and recommendations for future work.

## **2 LITERATURE REVIEW**

### ***2.1 Overview***

The world is currently in its early stage of undergoing dramatic change, all these are influence by the depletion of fossil fuels and the soaring increase average global temperature or global warming. To overcome with the situation implementing clean energy technology such as ethanol dry reforming for hydrogen production could save our world from the energy crisis and reduce pollution.

The process of taking CO<sub>2</sub> a harmful gas for the environment and making it into something more valuable is interesting and beneficial(Atashi H, 2010)(Pholjaroen B, 2009). There has been a lot of research and patents done on the subject but little is known and understands, clearly renewable energy is the key for our sustainable development.

### ***2.2 Introduction***

This chapter explained the history of fuel cells technology and how the basic device works. Next is describing advantages and disadvantages of how hydrogen is produce from both renewable and non-renewable sources. Lastly is the comparison of ethanol dry reforming versus ethanol steam reforming.

### ***2.3 Fuel Cells***

Fuel cells are devices that convert hydrogen (fuel) and oxygen (oxidant) into water along while generating electricity. It was first invented by a British scientist Sir William Robert Grove in the 19<sup>th</sup> centuries, he was experimenting electrolysis of water that let him to discovered the new technology (J. Laminie. 2003). During the time fuel cell technology was only for the purpose of space applications, since the cost of manufacturing the technology was quite high at the time. Fuel cells are electrochemical devices which will not be subjugated by thermodynamic laws of heat which is by combustion.

Hydrogen is fed in the anode where its electron is stripped thus ionized the hydrogen atoms. The ions then pass through a conductive electrolyte to combine with oxygen at the cathode. The negatively charged electrons provide the current through wires to do work. The electrolytes play a very important role by permitting only the appropriate ions to pass between the anode and cathode. There are a few types of electrolytes available in today markets that are proton exchange membrane (PEM), solid oxide alkali, molten carbonate and phosphoric acid (Smithsonian Institution. 2008). Basic overall reaction of fuel cell is shown below.



(Pilatowsky 2011)

## ***2.4 Hydrogen Production (renewable)***

### ***2.4.1 Electrolysis of Water***

Hydrogen produce by electrolysis is basically by running electricity through two electrodes in water, oxygen is gathered at the anode while hydrogen is at cathode. There are three type of industrial electrolysis two of which either bipolar or unipolar using aqueous solution of potassium hydroxide (KOH) and thirdly is a solid polymer electrolyte electrolyser. The production cost of the process is dependent on the economic factors of the electricity used. Other threats to the process are today's technologies are too small for high hydrogen demand and the electricity is generated by burning fossil fuels (Francois Leveque 2010).



### **2.4.2 Photolysis**

Hydrogen is produce by splitting hydrogen molecule from water compound by solar energy. A photoelectron-chemical cell used to carry out photoelectrolytis reactions that comprised of semiconductor to absorbs solar energy and produces electric energy used to separate water molecule. Integrating solar energy and water electrolysis into one single photoelectrode revolutionize the technology cutting the cost of power generator and electrolyzer. However phoelectrolysis is still in experimental stage and the cost is still very expensive for scale up (J.D. Holladay. 2009).

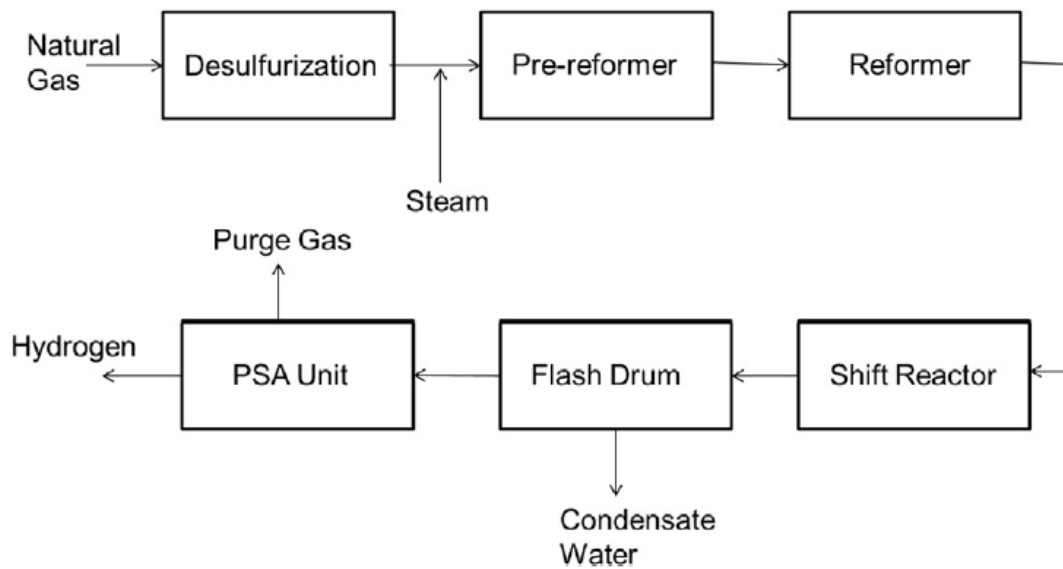
## **2.5 Hydrogen Production (non-renwable)**

### **2.5.1 Methane Steam Reforming**

Steam reforming of methane is the most study process, it is a catalytic process by reacting methane with steam in the presence of catalyst at high pressure and temperature to produce syngas of  $3\text{H}_2$  and  $\text{CO}$  (Rostrup-Nielsen, 1984). Nonetheless the process is an endothermic process, a huge amount of energy are been used making the process expensive. However, high quantities of carbon dioxide are emitted during the reforming processes. Besides that the raw product to obtain methane is from natural gas non-renewable resource therefore it is not a viable process for long term usage.



(Sofia D. Angeli. 2014)



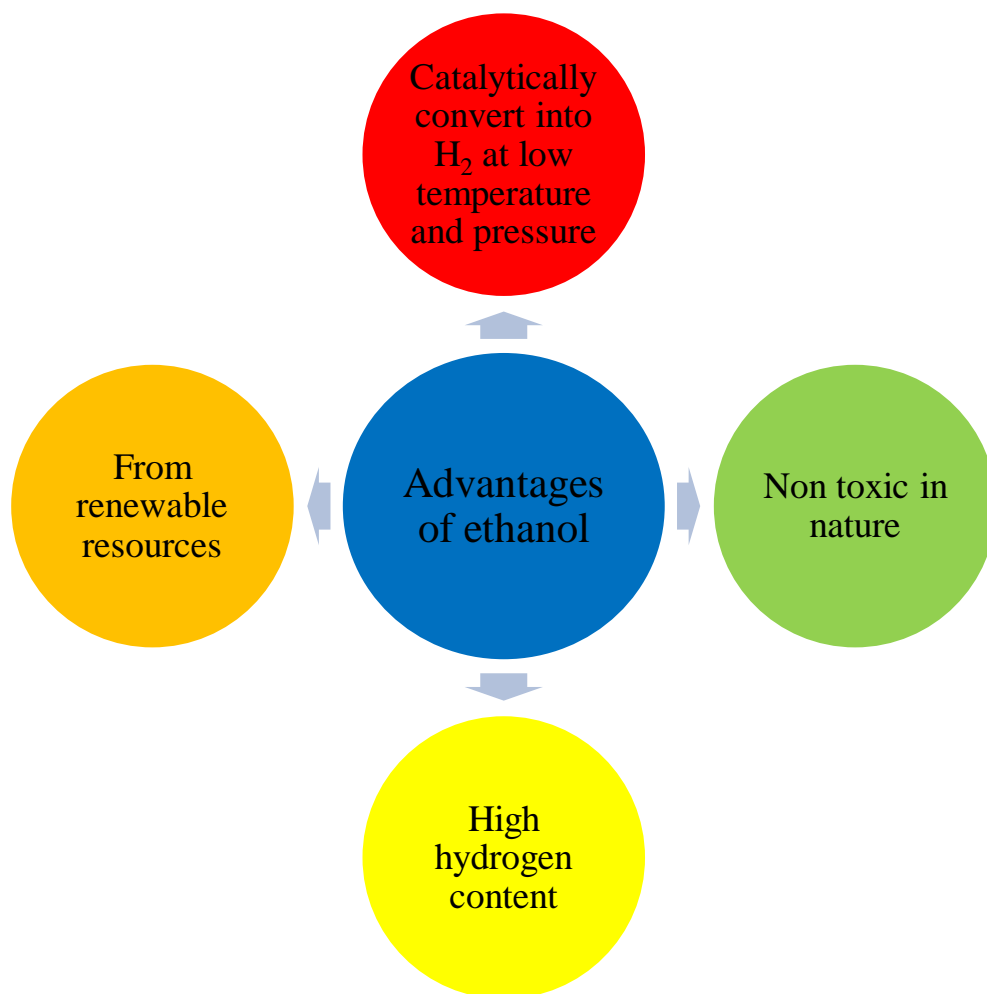
**Figure 2-1: Block flow diagram for steam methane reforming. (Mondal, 2014)**

### **2.5.2 Coal Gasification**

Gasification is a process of converting coal into syngas by partial oxidation in presence of steam, the technology been around since 1800. A gasifier converts hydrocarbon feedstock into syngas by applying heat under pressure. The coal is chemically broken apart due to the heat and pressure from the gasifier thus producing syngas. The main problems faced today with the process are water contamination and the harmful impact to the environment (land).

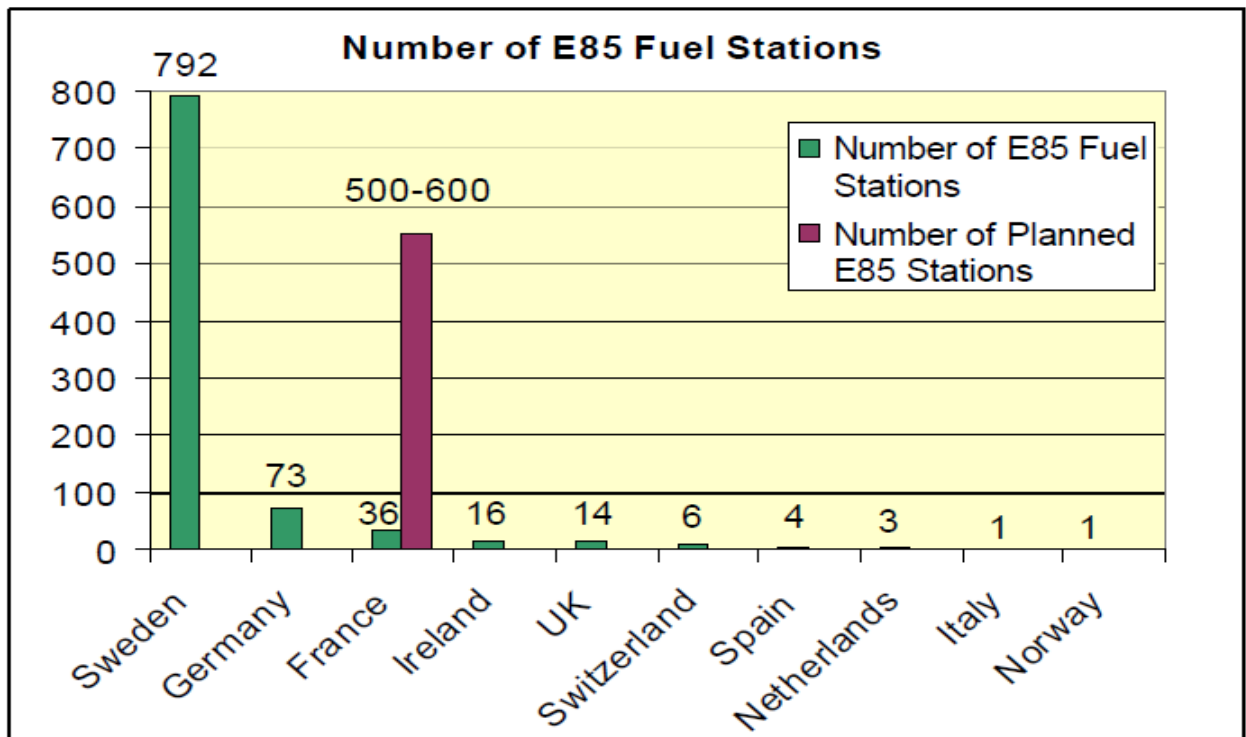
### **2.5.3 Bioethanol**

Bioethanol along with biodiesel has become one of the most promising biofuels today, in conjunction to uncertain fuel supply and efforts to reduce carbon dioxide emissions. Bioethanol is seen as a feasible fuel alternative because the source crops can be grown renewably by harvesting the energy of the sun in most climates around the world. This can be accomplish during the growing phase of the source crop, CO<sub>2</sub> is absorbed by the plant and oxygen is released in the same volume that CO<sub>2</sub> is produced in the combustion of the fuel.



**Figure 2-2: Advantages of ethanol in catalytic reaction**

Bioethanol in the modern day are being used as a biofuel for transport such as in Europe, where the country is blending 5% of ethanol with petrol. Other than that ethanol can be used in a number of chemical industries such as pharmaceuticals, cosmetics, beverages and medical sectors as well as for industrial. Improvement can be seen in the performance when ethanol is used as a substitute for lead as an oxygenating additive and has a high octane rating.



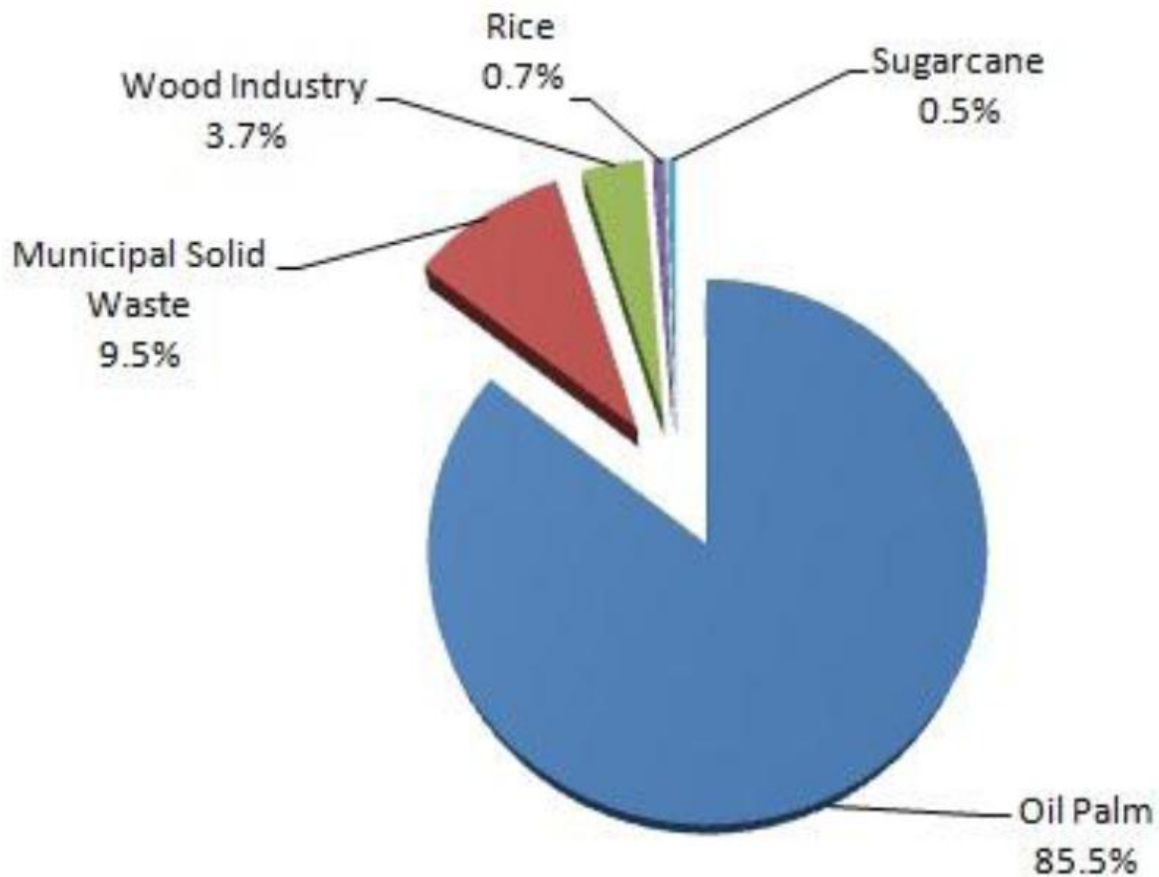
**Figure 2-3 : Number of E85 fuel stations in Europe countries**

The figure above shows leading Europe countries in bioethanol fuel stations. The highest number of fuel station is Sweden, follow by Germany. Meanwhile others countries are just starting on the new technology with lest that half of amount in Germany. Fuel cells are another potential area for ethanol use to produce heat and power. USA and Australia are the only two countries that managed to manufacture fuel cells technologies (Acumentrics made by USA and Ceramic Fuel Cells made by Australia) where bioethanol can be use straight away with the need of reformer to convert the ethanol to hydrogen gas. (Europa.eu)

## ***2.6 Malaysia Market for Bioethanol***

National Green Technology Policy was launched in 2009 by Malaysia Prime Minister Datuk Seri Najib Razak, the objective of this policy is to be a driver in the national economy and promote sustainable development. On the other hand the policy is in conjunction with Economic Transformation Programme (ETP) and Renewable Energy Act 2011. The function of Renewable Energy Act 2011 is to implement and establish a special tariff system to catalyze the generation of renewable energy and to provide any related matters. Overall the purpose of all the initiatives is to achieve the biomass industry potential.

In 2011 Malaysia launched National Biomass Strategy (NBS) 2020, an innovative on how to benefit from biomass for downstream activity in term of sustainable economic and social benefits. Malaysia has a big advantage when it comes to biomass, as the land is fertile for agriculture industry. Apart from that Malaysia is one of the world's largest producers of Crude Palm Oil (CPO) and generates about 12% of National Gross Income (NGI) from agriculture sector. Making it more lucrative, in 2012 it was estimated 83 million tonnes of dry biomass and expected to increase to 100 million tonnes by 2020. Among the 83 million tons of solid biomass (biomass (empty fruit bunches, fibers) and 60 million tons of palm waste liquid as a result of the production of palm oil, with 90% of this being discarded without being used.(Asiabiomass.jp)



**Figure 2-4: Malaysia H<sub>2</sub> prospect**

Being a second largest producer and exporter of oil palm in 2006, Malaysia's oil palm industry produced huge amount of biomass wastes that contribute about 85.5% of total biomass available in the country. To put in perspective Malaysia can generate up to RM 30 billion contribution to GNI by utilizing the biomass only from palm oil industry waste. This will also helps fellow Malaysians to have more and better jobs, estimated about 66 000 by 2020 together growing alongside with the industry. Malaysia has a solid track record in palm oil industry that produces a lot of usable waste thus putting Malaysia in the centre of the spotlight attracting international attention for its potential in sustainable source of biomass feedstock.

4 million hectares of land under oil palm plantation. 75% of total area planted is located in just four states, Sabah, Johor, Pahang and Sarawak, each of which has over half a million hectares under cultivation. (bioenergyconsult.com). The country is looking to lead Southeast Asia to turn agricultural waste into useful biofuel. Where else in Sarawak the opportunities start with 2<sup>nd</sup> Generation biethanol and Bio chemical production facility for sustainable feedstock supply for downstream operations. Agensi Inovasi Malaysia (AIM)

**Table 2-1: Advantages of hydrogen fuel cells**

High energy efficiency	Potential for a high operating efficiency (typically between 40% to 60% efficiency), and is not dependant on system size.
Scale of design	Highly scalable, modular and compact design based on power requirements.
Fuel/energy sources	Numerous types of potential fuel sources are available, mainly pure hydrogen, natural gas and methanol.
Moving/rotating components	The cell itself has no moving parts, allowing for quite and highly reliable operation.
Emissions	Produces zero or near-zero greenhouse emissions.
Recharge capability	Nearly instantaneous recharge capability compared to batteries.

A significant advantage of a hydrogen fuel cell is that only heat and water (or water vapour) is directly produced, eliminating the pollutants normally associated with combustion based power systems. Its green technology is an ideal replacement to conventional power systems as far as environmentalists are concerned. Besides that, fuel cells offer other unique advantages, such as summarized in Table 2-1.

## ***2.7 Ethanol steam reforming (ESR) versus Ethanol dry reforming (EDR)***

Ethanol is preferred because it is produced from a renewable source, safer and contains a higher number of hydrogen per molecule as compared to methanol and methane. In past few years there has been growing interest to produce hydrogen from clean renewable ethanol via steam reforming. However ethanol steam reforming is at disadvantage since the process is an endothermic that requires huge energy input to drive the reactions.



With the growing concern of environmental issues the selected process would have to meet the requirement. In a case of EDR it is preferred because even though steam reforming produces more  $\text{H}_2$  at the same time also producing  $\text{CO}_2$  however EDR is  $\text{CO}_2$  free. According to thermodynamics researched done by Wenju Wang ethanol dry reforming almost achieved complete conversion of 94.75-94.86% yield of hydrogen. The yield of hydrogen depends on the complex manner on process variables such as pressure, temperature,  $\text{CO}_2:\text{C}_2\text{H}_5\text{OH}$  ratio, etc.



(A. Zawadzki. 2014)